P 93

United States
Environmental Protection
Agency

Environmental Sciences Research
Laboratory
Research Triangle Park NC 27711

Research and Development

EPA-600/S7-81-092 July 1981

NEWARK PUBLIC LIBRARY

SEP 25 19c1

U. S. GOVT. PUBS.
DEPOSITORY 376

EPA

Project Summary

Secondary Formation Products in Power Plant Plumes

W. D. Balfour, L. O. Edwards, and G. K. Tannahill

Source and airborne measurements were made in October 1979, at the TVA Widows Creek Steam Plant in northeastern Alabama. Primary emissions from the flue gas stacks were determined including total mass, particle size distribution, SO_2, NO_x, and SO_3/H_2SO_4. An instrumented fixed wing airplane was used to acquire plume data at various altitudes and downwind distances. These data were used to establish secondary pollutant formation rates.

Sulfate transformation rates were measured between 4.3 percent hr^{-1} and 0.6 percent hr^{-1} for a well-defined plume at 1.1 hr and 2.2 hr plume ages respectively. A chemical element balance around the scrubber indicates that as much as 40% of the total mass exiting the scrubber was generated from entrained liquor. This accounts for 50% of the unit's sulfate emissions. These primary emissions account for between 4 and 17% of the total sulfates measured downwind in the plume.

This Project Summary was developed by EPA's Environmental Sciences Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The production of primary and secondary pollutants has been studied extensively in plumes of unscrubbed power plants, but only preliminary work has been done to determine effects of SO_2 scrubbers on downwind plume chemistry. There has been increased political pressure to reduce ambient sulfate levels by reducing sulfur dioxide emissions, the precursor to secondary sulfate particles, from coal-fired power plants. The principal strategies for reducing SO_2 emissions are the conversion to low sulfur coal or the installation of wet or dry SO_2 scrubbers in the plant stacks. Since the use of scrubbers allows burning higher sulfur coal, SO_2 scrubbing is likely to become more common in the future, as utilities use the more commonly available and less expensive higher sulfur coal.

In the past five years several studies have been conducted to determine the rate of sulfur dioxide to sulfate aerosol conversion in coal-fired power plant plumes. These studies indicated a conversion rate between 0 and 10% hr^{-1} for unscrubbed plants.

There is still uncertainty as to the formation mechanisms involved in the gas-to-particle conversion. Some studies obtained good correlation between formation rates and solar radiation, indicating the importance of gas phase free radical reactions. One of the main mechanisms for SO_2 oxidation, the reaction with hydroxyl radicals, the rate having been established in the range 0.4 - 2.7% hr^{-1}. Since the OH radical is formed photochemically, the conversion rate should show some dependence on solar intensity.

READEX FICHE

EP 1.89/2:

SO_2 oxidation may occur also on particle surfaces or in water droplets. Liquid phase oxidation may predominate under cloudy or high humidity conditions. Furthermore, metal salts in fly ash act as catalysts for SO_2 oxidation in water droplets. Therefore, the oxidation rate may be affected by any droplets produced by the scrubber and emitted from the stack.

Thus, the formation mechanism and the conversion rate in a scrubbed power plant plume may be different from those in an unscrubbed plume. This study addresses the questions of the nature of the primary emissions and the gas-to-particle conversion rates determined for a utility boiler equipped with a wet SO_2 scrubber.

To answer these questions, concurrent source and plume measurements were made. Source characterization measurements that were made included the following: EPA Method 5 for total mass, in-stack cascade impactor runs for particle size distribution, controlled condensation measurements for SO_3/H_2SO_4, continuous instrumental monitoring for SO_2, NO_x/NO and O_2, and collection of scrubber slurry and coal samples for elemental analysis.

The airborne measurements utilized the Pennsylvania State University Aerocommander 680E airplane equipped as follows: Environment One condensation nuclei counter, Thermo Systems 3030 Electrical Aerosol Analyzer, MRI 1550B integrating nephelometer, TECO Model 43 SO_2 analyzer, Meloy OA350 ozone monitor, and TECO Model 14D-E NO/NO_x analyzer. In addition, temperature, dew point, aircraft position, altitude and navigation were monitored routinely.

Two types of filters were used to sample plume particulates. Pretreated quartz filters (Gelman Micro-Quartz) were used with a high-volume air sampler to obtain aersol samples for sulfate and cation analysis by ion chromatography and inductively coupled argon plasma emission spectrometry. A tandem filter pack was used to obtain nitrate and nitric acid samples. The first filter was Teflon followed by a nylon filter (Ghia Corp.).

Results

Source Characterizations

The TVA Widows Creek Steam Plant is located 20 miles northeast of Scottsboro, Alabama and 30 miles southwest of Chattanooga, Tennessee. The plant has six wall-fired 135MW boilers (Units 1-6) ducted into a single 1000 foot stack. Two additional tangentially fired 557MW boilers (Units 7 and 8) are each ducted into individual 500 foot stacks. Each unit, except Unit 7, is equipped with an electrostatic precipitator with a design efficiency of 99.5 percent for fly ash removal. The precipitator on Unit 7 has a design efficiency of 90 percent. Ammonia (10 ppm) is injected into the flue gas to enhance collection efficiency for Unit 7. A limestone wet scrubber has been retrofitted downstream of the precipitator on Unit 8; the unit has a design efficiency of 80 percent for SO_2 removal. Units 1-6 burn a 0.8% sulfur coal, Unit 7 a 2.6% sulfur coal and Unit 8 a 4.1% sulfur coal.

A summary of the source characterization data is listed in Table 1. More extensive listings are available in the full report. Table 1 lists the range of values obtained during the testing program. The Project Report lists results on a daily basis. Inlet and outlet measurements across the scrubber or Unit 8 allowed a mass balance. Pertinent data is listed in Table 2. The scrubber can contribute mass through entrainment of scrubber liquor high in suspended or dissolved solids. This mass contribution can be calculated using the concept of chemical element balance. If one assumes that mass flow of species j from the scrubber, ϕ_j^{out}, is composed of material from the fly ash and scrubber liquor entrainment, then the mass

Table 1. Summary on Source Characterization Data

	Units 1-6	Unit 7	Unit 8	Unit 8B (Inlet)
EPA method 5 (gm/m^3)	—	1.52-3.20	0.009-0.021	5.61
SO_2 + SO_3 (ppm)	—	1663-1882	113-270	2051
Chemical Composition (% of a sample's total mass)				
F^-	—	0.002-0.007	<0.001	0.003
$SO_4^=$	—	0.370-0.933	25.70-26.20	0.812
Ca^{++}	—	0.268-1.208	3.49-7.32	0.660
Al^{+++}	—	1.54-4.63	3.95-4.13	2.28
Mg^{++}	—	0.091-0.318	0.349-0.478	0.106
Ti^{+++}	—	0.075-0.247	0.400-0.451	0.136
Particle size distribution (% Mass less than 2 μm)		7.9-15.3	20.7-53.2	10.9
Controlled Condensation				
H_2SO_4/SO_3 (ppm)	—	0.047-1.18	0.34-0.92	2.51-2.69
SO_2 (ppm)	—	1568-2242	258-269	2135-6300
Instrumental Gas Analysis				
SO_2 (ppm)	383-408	1543-1901	212-242	—
NO (ppm)	246-262	138-191	75-82	—
NO_2 (ppm)	0-19	4-13	—	—
O_2 (ppm)	10.5-11.5	7.2-8.5	13.5-13.5	—

Table 2. *Mass Balance Across SO_2 Scrubber Unit-8*

	Total	Ca^{++}	Mg^{++}	F^-	Al^{+++}	Ti^{+++}	$SO_4^=$
Mass Flow Into Scrubber (g/min), ϕ_j^{in}	188,500	4090	650	19	14,743	1056	5090
Mass Flow Out of Scrubber (g/min), ϕ_j^{out}	314	20.5	1.42	0.056	12.9	1.75	64.8
Scrubber concentration (g/l),C	—	0.700	0.140	<0.001	0.003	0.001	1.725

balance can be written as:

$$\phi_j^{out} = P\,\phi_j^{in} + C_j V$$

where ϕ_j^{out} = mass flow (g/min) of species j out of scrubber and into the stack.

P = penetration fraction of species j through scrubber

ϕ_j^{in} = mass flow (g/min) of species j into scrubber

C_j = concentration of j in scrubber liquor (g/l)

V = volume rate of scrubber liquor entrained (l/min)

A multiple variable regression analysis was performed on a set of six equations (one each for Ca, Mg, Al, F, Ti, SO_4) with three independent (ϕ_j^{out}, ϕ_j^{in} and C_j) and two dependent (V and P) variables. The resultant values that best fit the data were:

$V = 34.3 \pm 2.8$ 1/min

$P = 0.00097 \pm 0.00035$

The results indicate fly ash penetration through the scrubber is small, perhaps 0.1 percent.

Based on the above values, the mass flows of each species as well as the total can be calculated. Table 3 summarizes these results.

The predicted mass flow representing primary fly ash penetration is 183 gm/min. If the scrubber liquor mass flow is calculated by difference, the contribution is 131 gm/min. When the contribution is calculated by summing the individual species contribution, the result is 110 gm/min. Agreement (15 percent) is well within the expected experimental error.

From this analysis it can be concluded that of the particulate emissions from Unit 8, 40 percent are contributed by the scrubber itself (131 gm/min ÷ 131 + 183 gm/min). Also, greater than 90 percent of the sulfate emissions are generated by the scrubber (59.1 ÷ 64.0). Further analysis shows that the entrained mass from the liquor is mainly dissolved solids. This is evidenced by the sulfate-aluminum-calcium ratios in the particulate matter, which is similar to the solids dissolved and different from suspended solids ratio. Thus it can be expected that the scrubber generated mass will contribute to the fine particle size fraction.

Table 3. *Calculated Mass Flow Rate from Scrubber Unit*

	Total	Ca^{++}	Mg^{++}	F^-	Al^{+++}	Ti^{+++}	$SO_4^=$
Mass from Penetration (gm/min)	183	3.97	0.64	0.018	14.30	1.02	4.94
Mass from Entrainment (gm/min)	>86.6*	23.98	3.36	0.34	0.10	0.024	59.10

*This is the sum of the species measured.

Table 4. *Calculated Sulfate Formation Rates*

Flight #	$(SO_4^=/SO_2 + SO_4)x100$	Plume Age (hrs)	Rate Percent hr^{-1}
5	4.75	1.1	4.3
	1.27	2.2	0.6
6	14.6	0.6	24.3
	2.19	1.2	1.8
7	16.4	0.5	32.7
	8.84	0.6	14.7
9	5.59	0.2	28
	45	0.5	90
11	—	0.2	<0.3
	0.47	0.5	0.9

The levels of nitrate did not occur at values significantly above background

Plume Characterizations

Plume characterizations were based on results of plume cross-sectional analyses downwind of the plant. The distance was related to the travel time or plume age based on wind speed information furnished by the pilot balloon operators.

A summary of the calculated sulfate transformation rates is given in Table 4. The results were determined as follows: the sulfate values used in the numerator were obtained from hi-vol samples and were corrected for ambient background values. They were expressed as equivalent SO_2 volumetric concentrations. The SO_2 values in the denominator were the result of averaging measured SO_2 data (one observation per 0.5 second) over the period of hi-vol sampling. Plume ages were based on the downwind distance and wind speed.

Thus, no nitrate transformation rates could be determined. Based on limitations of sampling time and detection limit, the minimum transformation rate detectable for nitrate is 12 percent hr^{-1} Similar calculations for sulfate give a value of 0.3 percent hr^{-1}.

Several values listed in Table 4 are suspiciously high. The plant is located in a valley running approximately north to south. The prevailing wind during the study was from the west. Thus, after a brief travel time the plume impinged on the escarpment to the east. If significant SO_2 deposition occurred, then the denominator in the calculations would be erroneously low and the resultant transformation rates high. Many values calculated were an order of magnitude higher than the typical 1-10 percent hr^{-1} reported by other workers.

U.S. GOVERNMENT PRINTING OFFICE: 1981 -757-012/7208

Conclusions and Recommendations

The primary findings from this study are presented below.

The venturi scrubber besides being any effective flue gas desulfurization device (>90% removal) provided a high degree of control for particulates (>99.8% removal). Efficiency was lower for particles less than 2 μm in diameter.

As a result of the scrubber collection characteristics the emissions from the scrubbed stack exhibit a higher mass fraction of respirable particles (0.5) than from the unscrubbed unit (0.1). In terms of absolute emissions, the scrubbed stack in an order of magnitude less than the unscrubbed for particles less than 2 μm.

The scrubber tested did not efficiently remove SO_3/H_2SO_4 from the flue gas.

Analysis of the data showed that 40% of the total mass exiting the scrubber is generated from entrained liquor. This accounts for 90% of the sulfate emissions from the scrubber stack.

Sulfates emitted directly from the thru stacks account for between 4 and 17% of the total sulfates measured downwind.

Sulfate transformation rates were measured between 4.3% hr^{-1} and 0.6% hr^{-1} for well-defined plumes. Corrections for primary sulfate emissions were not significant.

Nitrate transformation rates could not be measured directly and are estimated to be less than 12% hr^{-1}.

As a result of this study, recommendations can be made in two areas: (1) development of sampling and analytical techniques and (2) considerations when selecting a site for plume studies.

In the sampling techniques there is a need for dependable real time continuous analyzers for sulfate and nitrate aerosols.

Site selection requires consideration of several parameters: history of the unit, constant load operation of the boilers, stable fuel source, preferably the same for all units, and local terrain effects.

*This Project Summary was authored by **H. M. Barnes**, who is also the EPA Project Officer (see below).*

The complete report, entitled "Secondary Formation Products in Power Plant Plumes," was authored by W. D. Balfour, L. O. Edwards, and G. K. Tannahill of Radian Corporation, Austin, TX.

The above report (Order No. PB 81-199 390; Cost: $9.50, subject to change) will be available only from:

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650

The EPA Project Officer can be contacted at:

Environmental Sciences Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

United States
Environmental Protection
Agency

Center for Environmental Research
Information
Cincinnati OH 45268

Postage and
Fees Paid
Environmental
Protection
Agency
EPA 335

Official Business
Penalty for Private Use $300